

THE EFFECT OF Fe ON Cr REDOX STATE IN SPINEL-SATURATED BASALTS: B. Hanson and J. H. Jones, SN-4, NASA, JSC, Houston, TX 77058.

Cr is thought to exist primarily as Cr^{3+} in basalts that crystallize under terrestrial redox conditions (QFM), and as Cr^{2+} under lunar conditions (IW-1). The different partitioning behavior of Cr^{2+} and Cr^{3+} in basalts is thought to be reflected in the generally higher Cr-content of lunar magmas in comparison to their terrestrial counterparts [e.g., 1]. The partitioning behavior of Cr in basaltic systems is, however, poorly understood. For example, [2] found that $D_{\text{Cr}}(\text{ol/liq})$ varied by a factor of 4 with T , $f\text{O}_2$, and liquid composition in Fe-free haplobasaltic systems. The change in $D_{\text{Cr}}(\text{ol/liq})$ was attributed to Cr changing valence state from Cr^{2+} to Cr^{3+} . In contrast, values for $D_{\text{Cr}}(\text{ol/liq})$ were found to be identical regardless of $f\text{O}_2$ in experiments performed in Fe-bearing systems [3,4]. The lack of variation of $D_{\text{Cr}}(\text{ol/liq})$ in the Fe-bearing systems led us to question whether Cr^{2+} exists in the presence of Fe^{3+} [e.g., 2,5]. We have performed a series of 1-atm experiments over large ranges of $f\text{O}_2$ designed to (1) evaluate the effect of Fe^{3+} on Cr redox state and (2) determine $D_{\text{Cr}}(\text{ol/liq})$ for both Cr^{2+} and Cr^{3+} .

Experimental Methods: Samples were hung in the hotspots of 1-atm furnaces on Pt loops. $f\text{O}_2$ was controlled by CO-CO_2 mixtures and monitored by a ZrO_2 oxygen sensor. Cr-loss to Pt at intermediate $f\text{O}_2$ (~QFM-IW) was minimized by performing multiple experiments on each loop in order to saturate the Pt loops with Cr. Volatile Cr-loss at high $f\text{O}_2$ (air) was minimized by running experiments in $\text{Pt}_{95}\text{Au}_5$ tubes open to atmosphere by a pin hole. Other samples were placed in graphite crucibles and sealed under vacuum in silica tubes, and suspended in 1-atm furnaces. Cr^0 was present in the graphite-capsule charges, and $f\text{O}_2$ is estimated to be less than 10^{-18} .

Results and Discussion: Fig. 1 shows the Cr content of the glass as a function of $f\text{O}_2$ for a set of experiments run on a composition in the Fe-free system FAD at 1320°C . All charges contained olivine and spinel. The Cr-content of the glass systematically decreases as the system is oxidized, reaching a minimum at an $f\text{O}_2$ of 10^{-3} . The Cr-content then begins to increase at higher $f\text{O}_2$. This behavior can be explained by a simple model. This increase in Cr has primarily been attributed to the increase in Cr^{2+} as the system is reduced [e.g., 6-8]. Because Cr^{3+} is an essential structural constituent of spinel, the Cr^{3+} -content of the liquid is "buffered" by spinel. The addition of more Cr^{3+} to the system results in spinel crystallization until the Cr^{3+} saturation abundance (CSA) is reached [8]. The CSA is independent of $f\text{O}_2$. This must be true because the spinel compositions do not change with $f\text{O}_2$. The increase in Cr as the system is reduced reflects the increasing $\text{Cr}^{2+}/\text{Cr}^{3+}$ in the liquid, which is externally buffered. The increase of Cr in the liquid as the system is oxidized is the result of the increasing abundance of Cr^{6+} . At $f\text{O}_2 = 10^{-3}$, where the Cr-content of the liquid is minimum, all of the Cr is trivalent, and thus represents the CSA. Using this model, the Cr^{2+} abundance be calculated for each experiment by simply subtracting the CSA from the total Cr. $\log[\text{Cr}^{2+}/\text{Cr}^{3+}]$, calculated from the data in Fig. 1, has been plotted vs. $\log f\text{O}_2$ in Fig. 2. The data form a line with a slope of 0.27, in agreement with the theoretically-predicted value of 0.25 for ideal reactions involving one electron [2].

We have applied the same logic to Fe-bearing systems to qualitatively evaluate the effect of Fe on $\text{Cr}^{2+}/\text{Cr}^{3+}$ in spinel-

saturated liquids using the high-Cr data from [8]. The Cr-content of Fe-bearing spinel-saturated liquids also decreases systematically with increasing $f\text{O}_2$ and that Cr in the liquid is buffered by spinel. Although spinel compositions do change with $f\text{O}_2$ in Fe-bearing systems, they remain surprisingly constant between IW and NNO [e.g., 6], then change very rapidly at higher $f\text{O}_2$. Thus, the Cr^{3+} content of the glass in the $f\text{O}_2$ -interval between IW and NNO should remain essentially constant. We are therefore constrained to assume that all Cr is trivalent at NNO because it is as far as we can deviate from IW without large changes in spinel composition. When $\log[\text{Cr}^{2+}/\text{Cr}^{3+}]$ is plotted vs. $-\log f\text{O}_2$, the data form a line with a slope that is very close to the theoretically-predicted value of 0.25. If all of the Cr in the liquid at NNO were not Cr^{3+} at NNO, as we have assumed, the slope of the would be shallower owing to an over-estimation of the Cr^{3+} -abundance. If the presence of Fe^{3+} changed $\text{Cr}^{2+}/\text{Cr}^{3+}$ by inhibiting Cr^{2+} , a shallower slope is predicted. The slope of approximately 0.25 suggests that the presence of Fe^{3+} does not preclude the presence of Cr^{2+} . It appears that Fe^{3+} suppresses Cr^{2+} so that it first appears ~3 log units of $f\text{O}_2$ less than in the Fe-free system.

The constancy in D_{Cr} in the Fe-bearing systems is simply due to similar values of $D_{\text{Cr}^{2+}}$ and $D_{\text{Cr}^{3+}}$. Figure 3 shows $D_{\text{Cr}}(\text{ol/liq})$ vs $\log f\text{O}_2$ for experiments spanning over 18 log units of $f\text{O}_2$ (FAD1). Since Cr^0 exists in the sealed-tube charges, it can reasonably be assumed that all of the Cr is Cr^{2+} , so $D_{\text{Cr}^{2+}}$ can be measured. Similarly, $D_{\text{Cr}^{3+}}$ is measured in the sample where all Cr is Cr^{3+} (i.e. $\log f\text{O}_2 = 10^{-3}$; Fig. 1). Also plotted in Fig. 3 are the values for Cr from experiments performed on two very different Fe-free compositions. Note that $D_{\text{Cr}^{2+}}$ and $D_{\text{Cr}^{3+}}$ are very similar in FAD1. D_{Cr} varies more with $f\text{O}_2$ in FAD2 and FAS, but all converge on a value of 0.6 ± 0.1 at low $f\text{O}_2$. Clearly $D_{\text{Cr}^{3+}}$ varies more with liquid composition than does $D_{\text{Cr}^{2+}}$ and, for some compositions, the two may be the same. In this latter situation, D_{Cr} will not vary with $f\text{O}_2$.

Our results bear on Cr^{2+} partitioning into spinel grown from basaltic liquids. It is thought that Cr^{2+} can not partition significantly into spinel because it cannot compete for sites with other divalent cations [9]. We propose that Cr^{2+} may be as compatible in Cr-spinel as Mg or Fe (i.e., $D_{\text{Cr}^{2+}}(\text{sp/liq}) = 1-2$), but the Cr^{2+} content of spinel is simply too low to measure accurately. For example, we calculate 1800 ppm Cr^{2+} in the FAD1 liquid at IW (Fig. 1). Cr^{2+} would contribute 0.18-0.32 wt.% Cr to a spinel containing >22 wt.% Cr, assuming a $D_{\text{Cr}^{2+}}(\text{sp/liq})$ of 1-2. It would be difficult to resolve this small amount of Cr^{2+} in spinel based on stoichiometry given analytical constraints. The problem becomes worse in Fe-bearing spinels in light of the assumptions regarding spinel stoichiometry and $\text{Fe}^{2+}/\text{Fe}^{3+}$ that must be made.

References: [1] Taylor, S.R. (1975) Lunar Science: A post-Apollo View. Pergamon, Elmsford, N.Y., 372pp. [2] Schreiber, H.D. and Haskin, L. A. (1976) PLPSC 7, p. 1221-1259. [3] Mikouchi et al. (1994) LPSC XXV, p. 907-908. [4] Gaetani, G.A. and Grove, T.L. (1996), in press. [5] Lauer, H.V. and Morris, R.V. (1976) J. Amer. Ceram. Soc. 60, pp. 443-451. [6] Murk, B.W. and Campbell, I.H. (1986) GCA, 50, pp. 1871-1887 [7] Maurel, C. and Maurel, P. (1984) Bull. Mineral. 105, pp. 640-647. [8] Hanson, B. and Delano, J.W. (1992) LPSC XXIII, pp. 481-482. [9] Mao, H.K. and Bell, P.M. (1975) GCA 39, pp. 865-874.

EFFECT OF Fe ON Cr REDOX STATE: B. Hanson and J. Jones

